Growth pathways in ultralow temperature Ge nucleation from Au

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Device integration on flexible or low-cost substrates has driven interest in the low-temperature growth of semiconductor nanostructures and in the fundamental mechanisms and limits of low-temperature growth. Catalytic growth of nanowires provides an ideal way to study these issues. In particular, Ge nanowires have been grown from Au via chemical vapor deposition at temperatures as low as 200 °C (Te is 363 °C for Ge-Au) via both vapor-liquid-solid (VLS) and vapor-solid-solid (VSS) mechanisms. [1, 2] But the nucleation of Ge directly from solid Au has not been observed.

We have therefore used in situ transmission electron microscopy (TEM) to examine the formation of the initial Ge nucleus at temperatures down to 150 °C. Observations were made in situ in an ultra high vacuum transmission electron microscope that has gas delivery capabilities. We start with either size-selected aerosol particles or with evaporated and agglomerated Au films on electron transparent SiN membranes. The samples are heated by direct current, and Ge is supplied by flowing the chemical vapor deposition precursor gases digermane through a capillary into the polepiece region. We use a combination of bright and dark field imaging conditions to characterize the structures present and to quantify phase stability as a function of the conditions.

Figs 1 (a-c) show three image sequences that track the progress of Ge nucleation from representative Au nanoparticles observed in plan-view at different temperatures and as a function of digermane exposure time. The Ge nucleation processes deduced from these and other sequences are shown schematically in Fig. 1 (d). Fig. 1 (a) is consistent with the VLS process. The Au particle transforms fully to a liquid AuGe alloy via a reaction front that moves inward from the surface; some time after this reaction is completed, solid Ge starts to precipitate. We observe this regime from well above Te to 100 °C below Te. From 270 to 200 °C we find an unexpected “mixed regime”, as in Fig. 1 (b). Solid Au starts to transform to liquid AuGe as a shell surrounding the Au. But before the Au has fully reacted, solid Ge nucleates. At the lowest temperatures (200−150 °C), an apparent VSS process occurs (Fig. 1 (c)). Here, the Au particles maintain flat facets and diffraction contrast consistent with a solid structure, but after some time Ge nuclei form at the edges of the particles. These data show that temperature is the main factor determining the reaction sequence.

Figs 2 (a-d) present kinetic measurements from each regime. In Fig. 2 (a, b) we show the two stages of the VLS regime. In the first stage, incoming Ge forms a surface layer of liquid AuGe that wets the Au, and the AuGe-Au boundary moves inward as the transformation continues. We find that the volume of solid Au decreases linearly with time, indicating a constant rate of Ge addition, [3] until a point (R_Au ~3.6 nm) at which the solid shrinks more rapidly and disappears. For the second stage, Fig. 2 (b), the amount of solid Ge in the liquid AuGe remains zero for a relatively long time, jumps rapidly, and then grows at a lower rate. The rapid jump provides an estimate [4] of the
supersaturation of Ge in AuGe required for Ge nucleation, which is strongly temperature dependent. For "VSS" regime (Fig. 2 (d)), nucleation from solid Au also requires an appreciable supersaturation (~4%) by assuming that Ge nucleates from the thin liquid AuGe shell that initially wets the Au. In the mixed regime (Fig. 2 (c)), the observed Ge jump volume is much larger (e.g., ~10% at 260°C) than expected from extrapolations of the supersaturation in the VLS and VSS regimes, (Fig. 2 (e)) because it reflects not only the prior supersaturation, but also the Ge that would be released by phase separation of Ge and Au.

From the above results and theoretical modeling, we understand that these complex reaction pathways are possible in even a simple binary eutectic system controlled by both kinetic and thermodynamic effects, while also suggesting the promise of catalytic growth for creating semiconductor nanostructures at low temperatures. [5]

References
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Fig.1. (a-c) Series of BF images showing the three different nucleation processes for Ge nanowire nucleation at varied temperatures; Schematics describing the three regimes of Ge nucleation.

Fig.2. (a, b) Kinetics of the transformation from solid Au to liquid AuGe, and of nucleation of Ge and its growth. (c, d) Kinetics of Ge nucleation and growth in the mixed and VSS regimes respectively. (e) The Ge nucleation jump volume as a function of T at a pressure of 1 × 10^{-6} Torr.